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THE APPLICATION OF SEM BY STRUCTURAL ANALYSIS OF COBALT ALLOYS

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ABSTRACT: Special alloys Co, Cr, W and C, which are presented in the literature like stellites can be classified into important cobalt alloys. The properties of stellites are influenced by chemical composition and the way of production very much. This paper describes material analysis of two components, which are used by mine of oil. These components are made from different kinds of stellites in every detail. During material analysis we performed analysis of chemical composition, rtg-phase analysis, dilatation test, measure of hardness and microstructure and microfractography analysis. Applications of SEM give us very important information, significantly supplement traditional materials analysis.

KEY WORDS: stellit, chemical composition, SEM

1. INTRODUCTION

Components used by petroleum production are in case of increasing content of hydrosulphide and sulfur in petroleum exposed to increasing corrosive attack. One of the ways to increase their lifetime is replacement of steels with other chemical resistive materials. Alloys Co, Cr, W and C called as stellites were successfully tested in operation. Materials called stellite 1, stellite 3, stellite 20 show high hardness (55-58 HRc), high abrasion and corrosion resistance, which is used in components like pump sleeves and rotary seal rings, wear pads, bearing sleeves, centreless grinder work – rests. All are available as castings and Stellite 1 and 20 are available for hardfacing [1]. Aim of this work is to describe results of material analysis of two components, which were parts of depth rod pumps.

2. COBALT AND ITS ALLOYS

Cobalt is polymorphic metal of white color, which looks like iron. It is recognized in two modifications. At normal temperature it crystallizes hexagonally with tightest configuration as α-cobalt. At temperatures close to 421 °C it changes to β-modification with cubic face centered lattice. According to small recrystallization heat in phase change, there comes to undercooling, resp. overheating of initial phase, and therefore both phases can coexist side by side in some spheres. In some cooling rate, martensitic transformation $\beta \rightarrow \alpha$ comes about. With creation of martensitic transformation, mutual coexistence of both phases can be demonstrated. At temperature close to 1015 °C cubic modification comes back to hexagonal.

Chrome, manganese, wolfram and molybdenum in solid state are dissolving to considerable measure, but at average content in alloys different intermediate phases occur, which complicate the steady states. Carbon in liquid Co is dissolving to concentration of 2.5 - 3 %. While Co doesn't create carbides, after its freezing there is a creation of carbide eutectic. In β phase Co is at eutectic temperature (approximately 1309 °C) dissolving about 1 percent of C, his solubility is decreasing with cooling. By 0.1 % content of C, temperature of change is close to 0 °C. Constitutional diagram of Co and Cr is known only partly, and different chemical reactions, which are running in solid state, are only slow and with imperfection. Cr is dissolving in Co at high temperatures to concentration of 30 - 40 %, but in change of β→α its solvability decreases to zero. Cr is dissolving at melting temperature in Co at 40 percent more concentration, at room temperatures its solvability decreases to 25 - 28 %. Some of their alloys are able to cure depending on chemical composition. Alloys of Co and Cr with 25 - 28 % Cr and 5 - 10 % Mo or W are hardly curable, and therefore they are manufactured by casting.

In technically important alloys of series WC-Co we can see following phases:

1. carbide of wolfram – WC,
2. solid solution of small W and C part in cobalt,
3. free graphite as undesirable part,
4. intermetallic thermal phase Co_3W_3C, **labeled as phase η.**

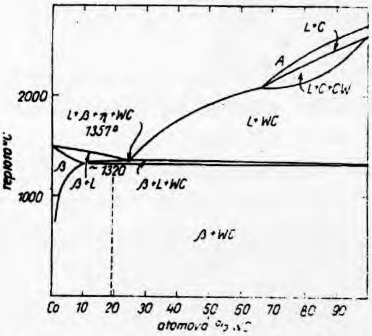

Fig.1: Constitutional diagram of W-Co-C

Figure 1 shows vertical look at constitutional diagram W-Co-C with region Co-WC for ratio WC to Co 57:43. At higher content of W, alloy solidifies at first with precipitation of WC and by reaching of eutectic composition with solidification of rest of the melting as eutectic. We can expect, that course of freezing with W and Cr together will be similar at contemporary secretion of WC and Cr from melted product. An interesting area in surround of eutectic temperature is showed in diagram, when in tight temperature intervals tight area of steady-state of phases exists: β-Co, WC a phase η.

According to Jareš, by content of 40 - 55 % Co, content of 20 - 35 % Cr, content of 10 - 15 % W and content of 1.5 - 3 % C these alloys aren't ductile, they mould the plate, which is consequently grinded. They are good polishers. They are thermally processed by stabilization longtime heating at temperatures of 650 - 800 °C. At thermal processing of alloys with higher content of C, there is a precipitation of carbides with maximal value of 750 °C, when mostly carbides M_7C_3, $M_{23}C_6$ and M_3C precipitate. At contents of C higher than 0.88 %, carbides occur also on grain bounds and as small carbides in the grains.

3. RESULTS OF ANALYSIS

Object with name "seating" is marked as sample 1 and "ball" is sample 2.

Relative mass Sample 1: 8.4946 g/cm^3 Sample 2: 8.7175g/cm^3

Chemical composition

Sample	C	Si	Ni	Fe	Co	Cr	W	Mn	Cu	V
1	2.63	0.81	1.97	2.58	44.89	30.67	12.25	0.32	Trace	Trace
2	2.64	0.38	1.88	2.73	40.26	31.44	17.50	0.41	Trace	Trace

RTG phase analysis

In sample 1 we found the phase β-Co with lattice parameter a = 3.544 Å without occurrence of α-phase. It is clear, that region of stability β-Co is moved to room temperatures, what was confirmed also by dilatometry test. Diffraction lines of phase Co_3W_3C were also found in RTG spectrum. Other lines, probably of $M_{23}C_6$ or M_6C, had weak intensity on strong background and we haven't been able to identify them exactly.

Dilatometry curve

Temperature program was from room temperature to 970 °C. There were allocated no transformation points at monitored temperature interval. The only thing that was found was abrasion of linearity at temperatures from 490 to 760 °C, coherent probably with carbides dissolving in cobalt matrix.

Hardness Sample 1: 58 - 58.5 HRc Sample 2: 59 - 59.5 HRc

Surface morphology

Surface of saddle has signs of lathe with measured displacement of cca 0.125 mm per turn, front and outer cylindrical area has signs of micro-relief surface after cutting. Morphology of sphere surface, evoking metallographic scratch pattern, suggests mechanical working with cutting and lapping, whereby we don't deny final electrolytic polishing (Figure 2).

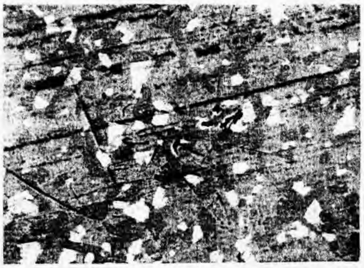

Fig. 2: Morphology of ball's surface (360x)

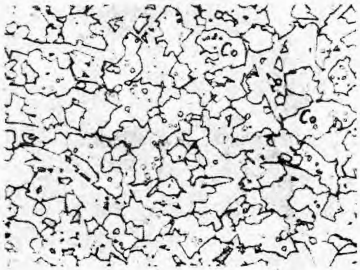

Fig. 3: Microstructure – SE mode (360x)

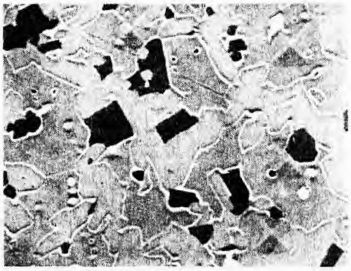

Fig. 4: Microstructure – BE mode (720x)

Structure

Results of microstructure evaluation didn't provide exact values. They have been observed after etching action with one of caustic dendrites directing to core of ball, with length approximately 4 mm and after usage of another caustic dendrite structure in her middle areas. We cannot make more significant dendrite type of macrostructure typical for moulding. In case of saddle, signs of dendrite structure haven't been observed, what could be caused by different shape of components.

We used combination of optical and scanning electron microscopy and EDX – microanalysis, as well as measuring of microhardness in HVm for microstructure evaluation. When using the combination of various special etchers, microstructure with gray phase in form of disordered sharp horizontal units has been generated (Figure 3). In its surrounding we could notice light phase, in which small sharp particles of gray phase occur. Membrane between these 2 phases looks like black. From analysis of steady-state diagram and micro toughness values it is clear, that light phase represents β-Co and gray phase carbides are on the base of W and Cr. After next etching done in β-Co, brown needles were observed, marked in literature as M_7C_3. With RTG analysis we detected that complex carbides $M_{23}C_6$ occurs probably on phase membrane Co and on carbides of W and Cr. On the other hand, SEM has shown us three basic structural elements (Figure 4). After application of caustic advised on WC, black grains have looked sharper, different than gray carbides of chrome. Cobalt phase has remained light.

Results of area and point EDX microanalysis have shown, that upper defined basic phase contains one of the elements Co, Cr or W. That is the reason why we tell about carbides of W, or Cr, that they are complex carbides. Cobalt matrix contains also W and Cr, probably with substitution dissolved. In SE regime β-Co looks like gray, intensively etched part, containing small particles or holes after them. Carbides of Chrome have similar color, but they are less etched. Carbides of wolfram look like light units (Figure 5). In BE regime are WC black, carbides of chrome are light gray and Co matrix dark gray, Figure 6. Complex carbides which are on grain boundaries β-Co appear in white coloration.

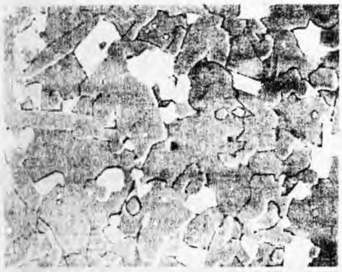

Fig. 5: Microstructure – SE regime (720x)

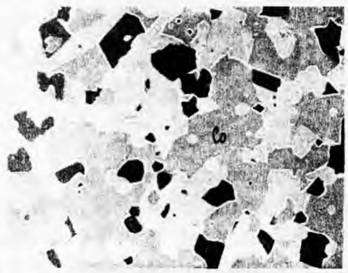

Fig. 6: Microstructure – BE regime (720x)

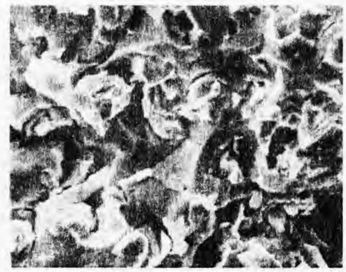

Fig. 7: Micromorphology of fracture (1080x)

We suppose that in solidification process impact carbides of wolfram act as crystallizing nukes for chrome carbides and after their process there is melt solidification surrounding. Presence of pores hasn't been observed.

Micromorphology of fracture

Fracture surface evidently has brittle character and suggests material fracture like sintered carbides with small content of binding material type. Fracture surface is continuing through phase boundary between carbides – cobalt matrix, respectively on the cleavage of carbides (Figure 7). The small ratio of ductile dimple failure rises to cobalt matrix failure.

4. CONCLUSIONS

On the basis of performed analysis we can suppose that analyzed components were with highest probability produced from cobalt alloys with firm mark Stellite 2 (seating) and Stellite 20 (ball).

Even the most specific signs prove solidification of liquid phase, i.e. the most frequently used technology of moulding, therefore we can't eliminate the application of supplementary technological process. Surface of ball was machined by treating and lapping process and probably by electrolytic polishing. Surface of saddle was gently turned and grinded. Both materials belong to group of non-hardening materials, what was proven also by dilatometry test. Possibly applicable application technologies of heat treatment are the solution annealing at temperatures of 1230 °C and ageing (650 - 900 °C) with inherent gradation of strength-plastic properties.

5. REFERENCES

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